ADVANCED STUDY FORUM "ADVANCED TECHNIQUES FOR ENERGY SOURCES INVESTIGATION AND TESTING"

SUMMARY

The Advanced Study Forum (ASF) was organised as an open discussion beyond the restrictions of the lectures and aimed at outlining the most suitable techniques for developing of advanced methods for portable and emergency systems testing and investigation – hot points, possibilities for by-passing equipment and methodological restrictions, amalgamation of techniques, trends in the market and research requirements, current solved and open problems. Some possibilities for bridging among sophisticated techniques such as X-rays diffraction, Vibrational and Ion-Beamed Spectroscopies, Electrochemical Impedance Spectroscopy, Scanning/Transmission Electron Microscopy, Synchrotron Radiation, etc., and real battery parameters and issues were summarised. Combined or individual methods like in-situ XRD and SEM/TEM, system integrated EIS devices and reference electrode techniques were evaluated as promising topics for future research and development. The ASF was a convenient platform for continuation of the short discussions during the lectures concerning the possibilities for application of the presented methods for related energy systems.

Chairman: Assoc. Prof. B. Monahov.

Participants: The lecturers and participants in the Workshop.

Abbreviations:

AEM - the active electrode material
ASF – Advanced Study Forum
EIS – electrochemical impedance spectroscopy
PCL – premature capacity loss
PCL 1 effect - a series of phenomena related to increased electric resistance
PCL 2 effect - a series of phenomena related to degradation of the positive active material
PCL 3 effect - a series of phenomena related to insufficient negative plate charge
S.O.C. – state of charge (of a battery)
S.O.H. – state of health (of a battery)
SEM – scanning electron microscopy
TEM – transmission electron microscopy
VRLA – valve regulated lead-acid batteries
XRD – X-ray diffraction

The discussion was opened by the Chairman - Ass. Prof. Boris Monahov from IEES.

I. B. Monahov (IEES) made a short **INTRODUCTION ON BATTERY TESTING METHODS.**

He listed the trends in emergency batteries testing, monitoring and diagnostics. The capacity (rated, actual, expected), cycle life (expected for the particular application profile), actual state of charge (S.O.C) and state of health (S.O.H.) were regarded as the main battery parameters to be controlled.

Two groups of testing methods were distinguished: invasive (electrolyte density determination and electrode potential measurements) and non-invasive (open circuit and float voltage measurement, battery/cell temperature monitoring, charge/discharge voltage measurement, DC current discharge, full or partial charge-discharge and AC pulses or impedance).

II. The Chairman made a **REVEW OF MAIN EMERGENCY BATTERIES PROBLEMS**

Antimony poisoning, PCL 1 and PCL 3 effects as well as grid expansion were considered as already solved battery problems. Among the still open ones following phenomena were considered: corrosion, passivation and sulphation, PCL 2 effect and active material shedding, insufficient recombination efficiency and thermal runaway effect. The controlled temperature charge and the total cell monitoring methods were outlined as possible ways to reduce some of the above problems.

III. P. Andreev (IEES) introduced some special features related to the **DYNAMIC ISSUES OF POTENTIOSTATIC CONTROL**

The electronic potentiostat is the most widely employed electronic instrument utilised for applications ranging from basic research to testing and evaluation of various electrochemical objects including POEMES. The electronic potentiostat function is to control the potential of the investigated electrode, measure the current at that electrode and operate without introducing neither static nor dynamic errors. The inherent “Ir” drop error due to the imperfect physical positioning of the reference electrode should be compensated for the sake of achieving the highest possible DC precision, which however affects the complex closed loop control system stability. In other words the potentiostat is possibly one of the few electronic instruments where DC precision is directly related to AC stability.

In order to dynamically neutralise the Ir compensation effect and restore the stable system operation a number of phase-stabilisation techniques are frequently applied yet these approaches inevitably deteriorate the measuring and control system dynamic properties. On the other hand the application of the emerging as a standard Electrochemical Impedance Spectroscopy (EIS) technique asks for faster instruments capable of measuring at higher operational frequencies while maintaining the essential DC accuracy. The classical arrangement of the general purpose instrument with its inherent limitation cannot be adopted to solve these two contradicting requirements.

A novel dual channel structure comprising of a cell with two counter electrodes and two split task DC and AC dedicated channels has been proposed. This innovative approach will facilitate the high frequency EIS application preserving both the fast AC response and the highest level of DC precision.

III. A. Momchilov (IEES) added in relation to Andreev’s information the **IMPORTANCE OF THE CHARGER** as a battery device**.**

Two parameters strongly depend on this device; the charge/discharge efficiency and the battery life (cycle life). Nowadays the quick charge is necessary in many cases and although reliable the battery needs additional voltage and battery temperature control during the charge process. It is very important especially for VRLA batteries, sealed Ni-MH batteries and Li-ion batteries. Both controls can insure safety and efficiently charge of the battery. Furthermore there is one important consideration that many people do not follow. It is necessary to charge the battery with its specified device. Thus the voltage and temperature control will be the necessary ones.

IV. Br. Banov (IEES*)* shared his experience on the issue of **HIGH TEMPERATURE TESTING OF LITHIUM SPINEL**

The problem is related to the increased working temperature of lithium batteries. Generally, the operating temperature range is –20^{o}C +40^{o}C, but in reality the upper temperature limit is widely surpassed. The real temperature beyond the windscreen of the car in summer exceeds 55^{o}C, even 75^{o}C! Thus it is imperative to develop lithium batteries capable to meet this requirement. The utilised cathode materials are subjected to this severe temperature test. The covering with MgO of the active electrode material (AEM) is proposed in the literature as solution of the problem. To replace the $LiCoO_2$ some non-toxic, environmentally friendly, low cost candidates with specific energy density close to 475 mWh.g-1 are under intensive investigation. The $LiMn_2O_4$ spinel is one of them, but the premature capacity loss is its significant disadvantage, especially at the elevated temperatures in the range of 30-60^{o}C. To overcome the problem the coating technique of the AEM is proposed. The stability of the AEM is enhanced in this way, but the electrochemical performances are deteriorated by 10-20%.

The speaker proposed a combination of the advantages of coated AEM, enhanced stability at elevated temperatures and long cycle life, with good electrochemical characteristics and high efficiency of the $LiMn_2O_4$ modified by ZnO as covering agent for solving the problem.

VI. P. Zoltowski (PAS) discussed the **IMPORTANCE OF USING SIMPLE MEASUREMENT TECHNIQUES** based on inserting reference electrodes into the cells for ***in-situ*** investigation of the charge and discharge processes as well as for determining the battery state of charge and state of health.

VII. I. Abrahams (Queen Marry College – UK) outlined the importance of the ***in situ*** **X-RAY DIFFRACTION TECHNIQUE** as a powerful method for investigating the changes in the crystal structure of battery active materials during operation and the perspectives for the further development of the method as a battery research tool.